

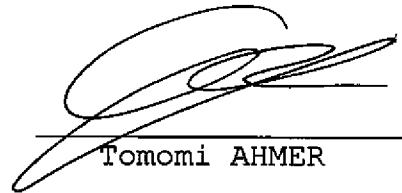
DECLARATION

I, Tomomi AHMER, a subject of Japan residing at 2-18, Kobai-cho, Kita-ku, Osaka-shi, Osaka 530-0038, Japan, solemnly and sincerely declare:

That I have a thorough knowledge of the Japanese and English languages; and

That the attached pages contain a correct translation into English of the priority document of Japanese Patent Application No. 260490/2002.

Signed this 29th day of February, 2008



Tomomi AHMER

[General Power

of Attorney No.]      9402017

[Necessity of Proof]      Needed

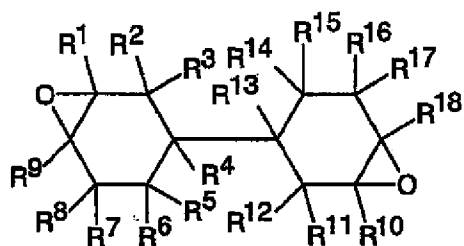
[Document Name]      Specification

[Title of Invention]      PROCESS FOR PREPARATION OF ALICYCLIC  
DIEPOXY COMPOUNDS

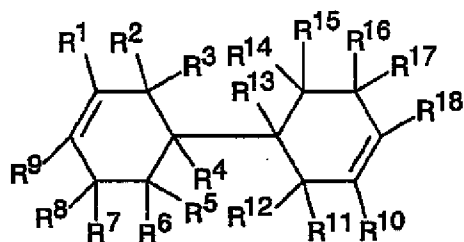
[Claims]

[Claim 1]      A process for preparation of an alicyclic  
epoxy compound represented by a general formula (I);

[Formula 1]



(I)



(II)

(wherein, each of R<sup>1</sup> to R<sup>18</sup>, which may be the same or different, represents a hydrogen atom, a halogen atom, a hydrocarbon group that may contain an oxygen atom or a halogen atom, or an alkoxy group that may have a substitutional group), characterized by comprising:

Epoxidizing an alicyclic olefin compound represented by a general formula (II) described above with an organic percarboxylic acid.

[Claim 2]    A process for preparation of an alicyclic epoxy compound according to claim 1, wherein the organic percarboxylic acid is obtained by oxidation of a corresponding aldehyde with oxygen, and the organic percarboxylic acid contains substantially no water.

[Claim 3]    A process for preparation of an alicyclic epoxy compound according to claim 1 or 2, wherein a water content of the organic percarboxylic acid is 0.8% by weight or less.

[Claim 4]    A process for preparation of an alicyclic epoxy compound according to claim 1, wherein the organic percarboxylic acid comprises peracetic acid.

[Claim 5]    A process for preparation of an alicyclic epoxy compound according to claim 4, wherein the peracetic acid comprises an ethyl acetate solution.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention pertains]

The present invention relates to a process for preparation of an alicyclic epoxy compound in which an unsaturated group-containing compound having a bicyclohexyl-3, 3'-diene skeleton is reacted with an organic percarboxylic acid.

[0002]

[Prior Art]

Currently, various types of epoxy compounds each having two alicyclic skeletons in the molecule are commercially available. Examples thereof manufactured by Daicel Chemical Industries, Ltd. include: 3,4-epoxycyclohexylmethyl-3'4'-epoxycyclohexanecarboxylate (CEL-2021); 1,2,8,9-diepoxy limonene (CEL-3000); one (CEL-2081) in which 3,4-epoxycyclohexylmethanol and 3,4-epoxycyclohexane carboxylic acid are coupled with both ends of an  $\epsilon$ -caprolactone oligomer through ester linkages. Cured products can be obtained by allowing such epoxy compounds to react with various curing agents and curing catalysts. A cured product of an epoxy resin is allowed to have good heat-resistance, transparency, and dielectric properties that are characteristics of a resin prepared from a compound with an alicyclic skeleton. Such an epoxy compound is useful as an ingredient to be included in coatings, adhesives, ink, and sealants, or as an intermediate to prepare any of other valuable compounds in a variety of end uses including pharmaceutical agents and medical supplies.

CEL-3000 has a methyl group on a carbon atom in the epoxy group so that the reactivity thereof is low due to its steric hindrance. Alternatively, since CEL-2021 or CEL-2081 has an ester group in the molecule, it has hydrolyzability. If they are used under high temperatures and high moistures or under

such a condition that a strong acid occurs, cured products thereof may suffer from decrease in physical properties.

Thus, an epoxy compound with an alicyclic skeleton having no ester group in the molecule has been desired.

In the non patent literature 1 mentioned below utilizes peroxyhydrate (where the peroxyhydrate means t-butylhydroperoxide) as an epoxidizing agent for synthesis of dicyclohexyl-3, 3'-diepoxide represented by the general formula (1) and molybdenum chloride (V) in a catalytic amount. In this literature, the peroxyhydrate is used at high temperatures above 80°C or more. Therefore, as the risk that the peroxyhydrate is explosively decomposed is involved, there is a problem in safeness. In addition, molybdenum chloride (V) used as a catalyst is expensive and strongly poisonous. Therefore, a preparation process that is economical and gives environmental consideration has been sought.

[0003]

[Non Patent Literature 1]

Russian Literature (Neftekhimiya, 1972, 12, 353.)

[0004]

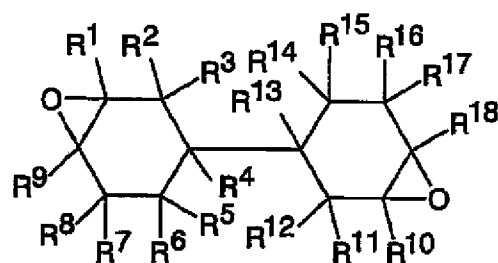
[Means for solving the Problems]

The inventors of the present invention have conducted an extensive study for attaining the above objects and have found that a highly pure epoxy compound can be economically obtained

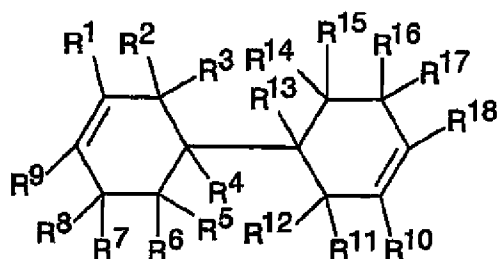
by using an organic percarboxylic acid in high yield. The present invention has been completed based on this finding.

That is, a first aspect of the present invention is a process for preparation of an alicyclic epoxy compound represented by a general formula (I):

[Formula 2]



(I)



(II)

(wherein, each of  $R^1$  to  $R^{18}$ , which may be the same or different, represents a hydrogen atom, a halogen atom, a hydrocarbon group that may contain an oxygen atom or a halogen atom, or an alkoxy group that may have a substitutional group), characterized by including:

epoxidizing an alicyclic olefin compound represented by a general formula (II) described above with an organic percarboxylic acid.



A second aspect of the present invention is a process for preparation of an alicyclic epoxy compound according to the first aspect of the present invention, in which the organic percarboxylic acid is obtained by oxidation of a corresponding aldehyde with oxygen, and the organic percarboxylic acid contains substantially no water.

A third aspect of the present invention is a process for preparation of an alicyclic epoxy compound according to the first or second aspect of the present invention, in which a water content of the organic percarboxylic acid is 0.8% by weight or less.

A fourth aspect of the present invention is a process for preparation of an alicyclic epoxy compound according to the first aspect of the present invention, in which the organic percarboxylic acid is peracetic acid.

A fifth aspect of the present invention is a process for preparation of an alicyclic epoxy compound according to the fourth aspect of the present invention, in which the peracetic acid is an ethyl acetate solution.

[0005]

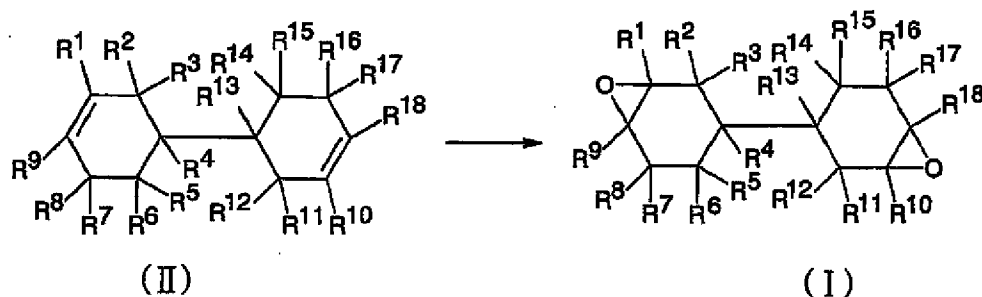
[Mode for carrying out the Invention]

An epoxy compound represented by the general formula (I) having an alicyclic skeleton in the present invention is prepared by oxidation of an unsaturated compound having a

bicyclohexyl-3,3'-diene skeleton represented by the general formula (II) with an organic percarboxylic acid.

[0006]

[Formula 3]



In the general formula (I) and the general (II), each of  $R^1$  to  $R^{18}$ , which may be the same or different, represents a hydrogen atom, a halogen atom, a hydrocarbon group that may contain an oxygen atom or a halogen atom, or an alkoxy group that may have a substitutional group.

The above unsaturated compound having a bicyclohexyl-3,3'-diene skeleton is generally synthesized by dehydration of a compound with a hydroxyl group. A preparation process in which such an unsaturated compound is synthesized from a compound having a cyclohexanol structure is described in "Synthesis and Reaction of Organic Compounds (I) ," pp.114-127, Shin-Jikken Kagaku Koza 14, JP 58-172387 A, JP 2000-169399 A, and so on.

[0007]

According to the present invention, the alicyclic epoxy compound can be prepared by the reaction of an unsaturated compound having a bicyclohexyl-3,3'-diene skeleton with an organic percarboxylic acid.

In the preparation process of the present invention, the organic percarboxylic acid (the organic percarboxylic acid refers to performic acid, peracetic acid, perbenzoic acid, perisobutyric acid, trifluoroperacetic acid, etc.) can be used as an epoxidizing agent. Of the organic percarboxylic acids, specifically peracetic acid is a preferable epoxidizing agent because of its reactivity, as well as high stability, required for preparing the alicyclic epoxy compound in the present invention.

Of those, it is preferred to use an organic percarboxylic acid substantially containing no water, specifically with a water content of 0.8% by weight or less, preferably 0.6% by weight or less in order to obtain a compound having a high epoxidation rate. In the present invention, the organic percarboxylic acid substantially containing no water is prepared by the air oxidation of aldehydes, for example acetaldehyde. For instance, peracetic acid is prepared by a process as described in German Patent Application Publication No. 1418465 or JP 54-3006A. According to this process, in comparison with a process of synthesizing an organic

percarboxylic acid from hydrogen peroxide followed by extraction by a solvent to produce an organic percarboxylic acid, an organic percarboxylic acid having high concentration can be synthesized continuously in a large amount and can be therefore obtained at a substantially low price.

[0008]

Although there is no strict limitation on the amount of the epoxidizing agent, the optimum amount in each case is determined depending on variable factors such as the reactivities of individual epoxidizing agents and alicyclic olefin compounds used, and the epoxidation rate of interest.

The epoxidation reaction is performed by adjusting the use or unused of a solvent and reaction temperature in accordance with an apparatus and the physical properties of raw materials. A solvent can be used for the purposes of reducing the viscosity of raw materials, stabilizing the epoxidizing agent by dilution, and so on. Esters, aromatic compounds, ethers, and the like can be used in the case of peracetic acid. A specifically preferable solvent is ethyl acetate, hexane, cyclohexane, toluene, benzene, or the like. Of those solvents, ethyl acetate is specifically preferable. The reaction temperature is determined depending on the reactivity of an epoxidizing agent and an unsaturated group-containing compound utilized.

For example, if peracetic acid that is a preferable epoxidizing agent is used, the reaction temperature is preferred to be at 20 to 70°C. The reaction is slow at temperatures less than 20°C, and peracetic acid is decomposed with heat generation at temperatures beyond 70°C, which is not preferable.

[0009]

The molar ratio for preparing the epoxidizing agent relative to unsaturated bond can be varied depending on how much unsaturated bond is desired to remain, and so on. If a compound having a high epoxidation rate is demanded, preferably 1.0 to 3.0 mol, more preferable 1.05 to 1.5 mol of the epoxidizing agent is added based on 1 mol of an unsaturated group. In general, the epoxidizing agent beyond 3.0-fold mol is disadvantageous in view of cost efficiency and side reaction. According to the preparation process of the present invention, there is no need to use any expensive epoxidizing agent or catalyst.

[0010]

A crude solution obtained from the reaction does not require any specific manipulation. For example, the crude solution may be aged while agitating for 1 to 5 hours. Appropriate methods for isolation of the epoxy compound from the resultant crude solution include a method of precipitating the epoxy compound with a poor solvent, a method of putting the epoxy compound into

hot water under agitation to remove the solvent by distillation, and a method of directly eliminating the solvent.

[0011]

The alicyclic epoxy compound represented by the above general formula, which is produced in the preparation process of the present invention, is able to produce various coatings, ink, adhesives, sealants, or molded products, or an intermediate for other applications using such an alicyclic epoxy compound, through single polymerization or copolymerization, or by further reacting with other compounds. Examples of the end uses employing the alicyclic epoxy compound represented by the above general formula (I) include: agents for removing oxygen; coatings for furniture decorative coatings; coatings for beverage cans and the other cans; adhesives; undercoatings for automobiles; sealers; finishings; inks for textual information or image information; sealants for electronic parts; photoresists suitable for developing printing plates or printed circuit boards; casting rolls for printing; glass composed mainly of unsaturated polyester and styrene; moldings of molding blends or sheet-forming blends reinforced with carbon, graphite, or other fibers; solvents; flame retardants; and intermediates to prepare other valuable compounds in various end uses including pharmaceutical products and medical supplies.

In addition, the alicyclic epoxy compound represented by the above general formula (1) is allowed to have heat-resistance, transparency, and good dielectric properties that are characteristics of a resin using a compound having an alicyclic skeleton.

[0012]

[Examples]

The following examples are used for illustrations of the present invention, and they do not restrict the scope at all.

[Example 1]

In a reactor, 406 g of bicyclohexyl-3,3'-diene, which is an alicyclic olefin compound represented by the above general formula (II), and 1,217 g of ethyl acetate were placed. While nitrogen was flown into a gas phase part and the temperature in the reaction system was controlled at 37.5°C, 457 g of an ethyl acetate solution (water content: 0.41% by weight) containing peracetic acid at 30% by weight was added dropwise for about 3 hours. After completion of dropwise addition of the peracetic acid solution, the resulting mixture was aged at 40°C for 1 hour to complete the reaction. The crude liquid at the completion of the reaction was then washed with water at 30°C, and treated at 70°C/20 mmHg to remove low-boiling-point compounds. Consequently, 415 g of an epoxy compound was obtained with an yield of 85%.

The oxirane oxygen content of the epoxy compound obtained was 14.7% by weight (theoretical value: 16.5% by weight).

In  $^1\text{H}$ NMR analysis, a peak at about  $\delta$ 4.5 to 5 ppm originating from the inner double bond disappeared, and the formation of a proton peak at about  $\delta$ 3.1 ppm originating from the epoxy group was observed. It was confirmed that the epoxy compound was an alicyclic epoxy compound represented by the above general formula (I). Figure 1 shows the NMR chart of the obtained alicyclic epoxy compound.

[0013]

[Example 2]

243 g of bicyclohexyl-3,3'-diene, which is an alicyclic olefin compound represented by the above general formula (II), and 730 g of ethyl acetate were placed. While nitrogen was flown into a gas phase part and the temperature in the reaction system was controlled at 37.5°C, 274 g of an ethyl acetate solution (water content: 0.41% by weight) containing peracetic acid at 30% by weight was added dropwise for about 3 hours. After completion of dropwise addition of peracetic acid solution, the resulting mixture was aged at 40°C for 1 hour to complete the reaction. The crude liquid at the completion of the reaction was then washed with water at 30°C, and treated at 70°C/20 mmHg to remove low-boiling-point compounds. Consequently, 270 g of an epoxy compound was obtained with an yield of 93%.



The oxirane oxygen content of the epoxy compound obtained was 15.3% by weight.

IN  $^1\text{H}$ NMR analysis, a peak at about  $\delta 4.5$  to 5 ppm originating from the inner double bond disappeared, and the formation of a proton peak at about  $\delta 3.1$  ppm originating from the epoxy group was observed. It was confirmed that the epoxy compound was an alicyclic epoxy compound represented by the above general formula (I).

[0014]

[Comparative Example 1]

25 g of bicyclohexyl-3,3'-diene, which is an alicyclic olefin compound represented by the above general formula (II), and 20 g of ethyl acetate were placed. While nitrogen was flown into the gas phase part and the temperature in the reaction system was controlled at 60°C, 36 g of hydrogen peroxide solution at 30% by weight was added dropwise for about 1 hour. After the completion of dropwise addition of hydrogen peroxide solution, the resulting mixture was aged at 60°C for 12 hours to complete the reaction.

In  $^1\text{H}$ NMR analysis of the reaction crude liquid, the peak at about  $\delta 4.5$  to 5 ppm originating from the inner double bond did not disappear, and the formation of a proton peak at about  $\delta 3.1$  ppm originating from the epoxy group was not observed. No

alicyclic epoxy compound represented by the above general formula (I) was formed.

[0015]

[Comparative Example 2]

25 g of bicyclohexyl-3,3'-diene, which is an alicyclic olefin compound represented by the above general formula (II), 135 g of benzene, and 0.07 g of molybdenum pentachloride as a catalyst were placed. While nitrogen was flown into the gas phase part and the temperature in the reaction system was controlled at 80°C, 120 g of benzene solution containing t-butyl hydroperoxide at 30% by weight was added dropwise for about one hour. After the completion of dropwise addition of benzene solution containing t-butyl hydroperoxide, the resulting mixture was aged at 80°C for 3 hours to complete the reaction. The crude liquid at the completion of the reaction was then washed with water at 30°C, and treated at 70°C/20 mmHg to remove low-boiling-point compounds. 25.3 g of an epoxy compound was obtained with an yield of 84.6%.

The oxirane oxygen content of the epoxy compound obtained was 12.6% by weight.

IN <sup>1</sup>HNMR analysis, the peak at about δ4.5 to 5 ppm originating from the inner double bond disappeared, and the formation of a proton peak at about δ3.1 ppm originating from the epoxy group was observed. Though it was confirmed that the

epoxy compound was an alicyclic epoxy compound represented by the above general formula (I), it was also confirmed that the yield of the alicyclic epoxy compound obtained was low compared with Examples 1 and 2, and the oxirane oxygen content was also low.

[0016]

[Effect of the Invention]

According to the present invention, the highly pure alicyclic epoxy compound represented by the general formula (I) can be produced from an alicyclic olefin compound, in high yield and at low cost.

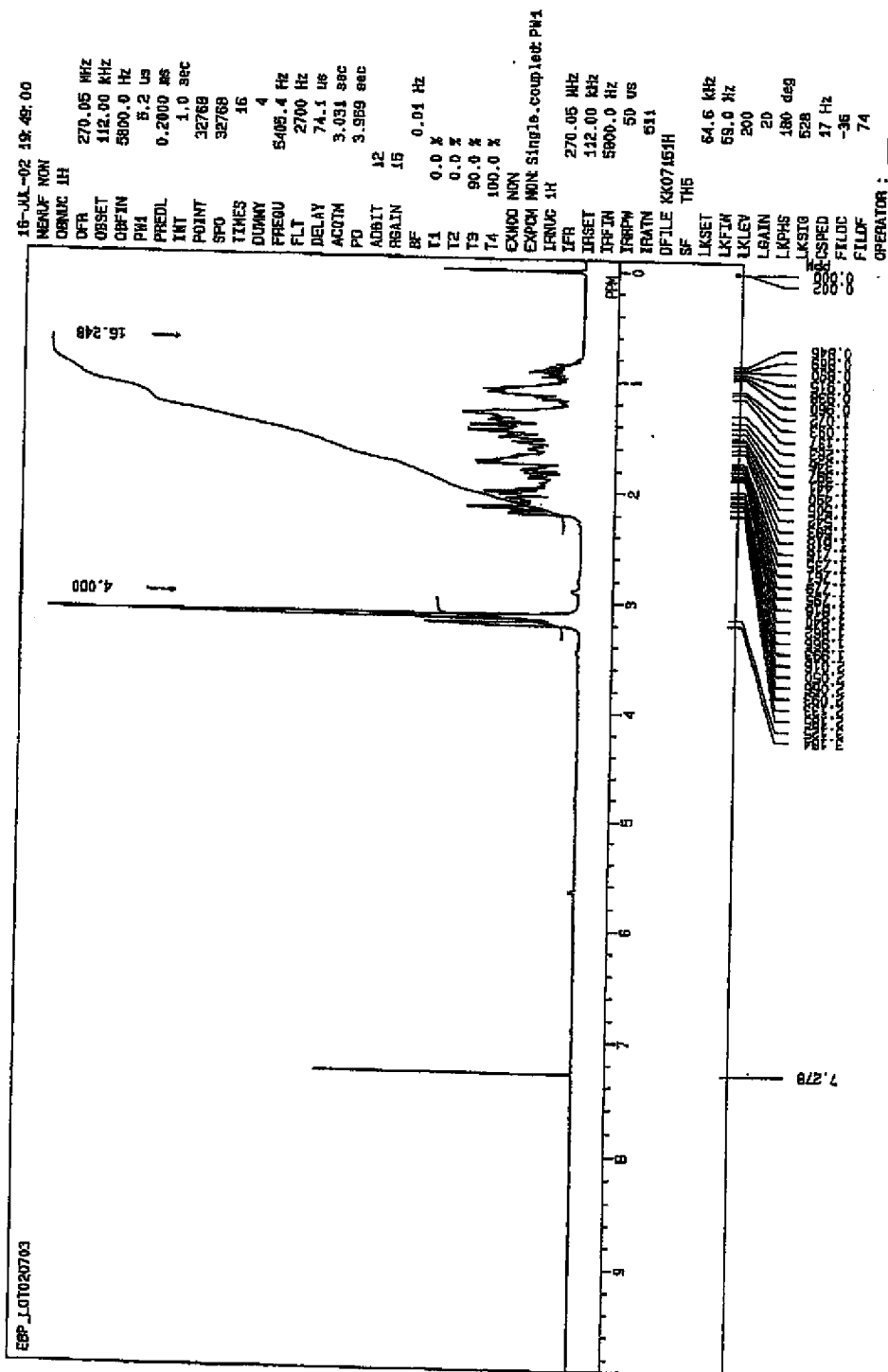
[Brief Explanation of the Drawing]

[Figure 1]

Figure 1 is the NMR chart of the alicyclic epoxy compound obtained in the example 1.

[Document Name] Drawing

[Figure 1]



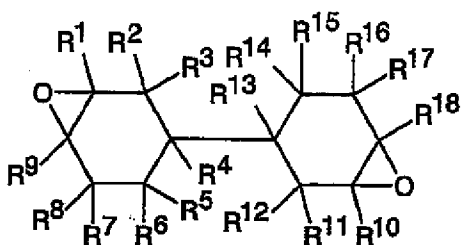
[Document Name] Abstract

[Abstract]

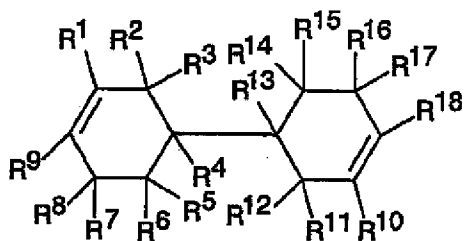
[Objects] To provide an efficient and economical process for epoxidization of compounds containing unsaturated group.

[Means for Solving Problem] A process for preparation of an alicyclic epoxy compound represented by a general formula (I);

[Formula 1]



(I)



(II)

(wherein, each of R<sup>1</sup> to R<sup>18</sup>, which may be the same or different, represents a hydrogen atom, a halogen atom, a hydrocarbon group that may contain an oxygen atom or a halogen atom, or an alkoxy group that may have a substitutional group), characterized by comprising:

Epoxidizing an alicyclic olefin compound represented by a general formula (II) described above, with an organic percarboxylic acid.

[Selected Figure]      None